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(54) Title: PHOTO-POLYMERS AND USE THEREOF

(57) Abstract: The present invention provides an optical polyacrylate polymer wherein at least 20 % w/w of the total monomer repeating units are of the general formula (I): $-(CH_2-C(R^1)(COOR^2))-$ wherein R^1 is H or a C1 to C12 aliphatic and/or aromatic group, and R^2 is an aliphatic and/or aromatic moiety containing at least one S atom. In further aspects, the present invention provides methods of making the above polymers, as well as planar lightwave circuits formed from such polymers.

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PHOTO-POLYMERS AND USE THEREOF

The present invention relates to optical polymers and the use thereof.

5

Large-scale integration of various electronic components on single chip was responsible for the microelectronic revolution we have witnessed. The same argument justifies the need for the integration of photonic components on a single substrate.

10 Such integrated photonic devices are also termed as planar lightwave circuits (PLCs) [1]. Synthetic plastics polymers are one of the very promising alternatives for the fabrication of PLCs. Polyimide [2], polycarbonate [3], cyclobutene [4,5] and poly-acrylate [6,7] are examples of the polymers being
15 explored for such applications.

Poly methyl methacrylate (PMMA) is one of the acrylate materials that has been very well explored in the context of polymer optical fibres [8] and planar waveguides [9,10,11,12].

20 The advantages of PMMA are its well-understood chemistry, cost effective precursors and low temperature processing.

Furthermore, it has reasonably good transmittance properties with acceptable losses at wavelengths up to 850 nm. However, its limited temperature stability and increased losses for
25 wavelength windows of 1.3 and 1.55 μ m make it unsuitable for telecommunication applications. It has been found that the losses in 1.3 and 1.55 μ m wavelength range can be reduced to some extent by the partial substitution of hydrogen groups with deuterium or fluorine. The problem of limited temperature
30 stability however remains. Furthermore, control of viscosity is needed for various applications requiring thick films (like multimode components and tall flip chip bumps).

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We have now found that, surprisingly, it is possible to produce economically, polyacrylate optical polymers with very high thermal stability, typically up to 250°C or more, with a good range of refractive index and viscosity, and good
 5 adhesion to typical substrates such as glass, silica and silicon, which polymers are based on sulphur containing monomers.

Thus in a first aspect the present invention provides an
 10 optical polyacrylate polymer wherein at least 20% w/w of the total monomer repeating units are of the general formula (I)



wherein R^1 is H or a C1 to C12, preferably C1 to C6, aliphatic or aromatic group, most preferably CH_3 , and

15 R^2 is an aliphatic and/or aromatic moiety containing at least one S atom, and preferably is of the general formula R^3SR^4 wherein R^3 and R^4 are the same or different and each is selected from: an aliphatic group $\text{C}_n\text{H}_{2n+1}\text{--yZ}_y$ wherein n is an integer from 1 to 12, preferably from 1 to 6 (such as methyl,
 20 ethyl, propyl, butyl, pentyl, hexyl, cyclohexyl), the or each Z can be F, Cl, Br or I, and y can be from 0 to 2n+1, and an aromatic group $\text{C}_6\text{H}_5\text{--xA}_x$, wherein the or each A can be F, Cl, Br, I, or (meth)acrylate, preferably F, Cl, Br, or I, and x is a natural number from 0 to 5, preferably zero. Preferred
 25 examples of R^2 are $(\text{C}_6\text{H}_5)\text{S}(\text{CH}_2)$, $(\text{C}_6\text{H}_5)\text{S}(\text{C}_2\text{H}_4)$, $(\text{C}_6\text{H}_5)\text{S}(\text{C}_6\text{H}_4)$, $(\text{CH}_3)\text{S}(\text{CH}_2)$, $(\text{CH}_3)\text{S}(\text{C}_2\text{H}_4)$, $(\text{CH}_3)\text{S}(\text{C}_6\text{H}_4)$, $(\text{C}_2\text{H}_5)\text{S}(\text{CH}_2)$, $(\text{C}_2\text{H}_5)\text{S}(\text{C}_2\text{H}_4)$ and $(\text{C}_2\text{H}_5)\text{S}(\text{C}_6\text{H}_4)$.

As indicated above, one or more of R^3 or R^4 may themselves
 30 contain further acrylate and/or methacrylate groups, which lead to multi functionality and can be used to obtain cross-linked photopolymers. Further preferred examples of R^2 of this type include: $(\text{CH}_2)\text{S}(\text{CH}_2)\text{--OOC--C(R}^1\text{)=CH}_2$, $(\text{C}_2\text{H}_4)\text{S}(\text{C}_2\text{H}_4)\text{--OOC--C(R}^1\text{)=CH}_2$ and $(\text{C}_3\text{H}_6)\text{S}(\text{C}_3\text{H}_6)\text{--OOC--C(R}^1\text{)=CH}_2$. Increased cross-

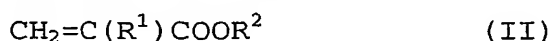
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linking has the advantage of increasing density and mechanical strength, as well as improving impermeability to moisture and resistance to other potentially damaging environmental factors.

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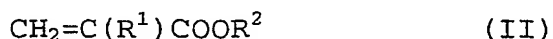
Whilst polymers produced using conventional acrylates typically have T_g (glass transition temperature) values of around 100 to 120°C, polymers according to the present invention can readily be obtained with significantly higher T_g values of around 180°C. In general the polymers of the present invention have T_g values of at least 140°C, and typically from 160 to 200°C. Also whilst the thermal stability limit of polymers produced using conventional acrylates is only around 220 to 250°C, the polymers of the present invention generally have good thermal stability up to at least 280°C, for example, up to around 300°C.

In another aspect the present invention provides an optical polyacrylate polymer obtainable by polymerisation of acrylate monomer wherein at least 20% w/w of the acrylate monomer is of the general formula (II)



wherein R^1 and R^2 have the same meaning as before.

25 In a further aspect the present invention provides a photo-polymerisable composition comprising acrylate monomer in intimate admixture with a photo-initiator, wherein at least 20% w/w of the acrylate monomer is of the general formula (II)



30 wherein R^1 and R^2 have the same meaning as before.

In a yet further aspect the present invention provides a process for producing a polyacrylate photo-polymer comprising the steps of :

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providing a photo-polymerizable composition of the invention, and exposing said composition to light so as to activate the photo-initiator.

5 Thus the present invention also provides a method of producing a PLC which comprises the steps of :
applying a photo-polymerisable composition of the invention to a substrate;
projecting a photographic image defining components of said
10 PLC onto said composition so as to photo-polymerise selected portions of said composition; and
removing unreacted composition from said substrate.

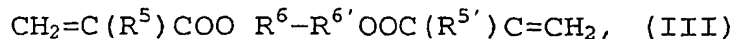
In a still further aspect the present invention provides a PLC
15 wherein the circuitry is of a polymer of the present invention.

It will be appreciated that various other acrylate monomers and non-acrylate monomers suitable for use in the production
20 of optical polymers, may also be included in the polymerisable compositions for various purposes, such as in order to extend the sulphur containing acrylate monomer with lower cost monomers, and/or to modify the optical and/or other physical properties of the polymers provided by them. Thus for example
25 by using suitable proportions of two different monomers which when used alone provide polymers with different refractive indices, it is possible to obtain polymers with various intermediate values of refractive index. Of course more than two monomers may be used, the refractive index of the final
30 product corresponding generally to the weighted average of the individual refractive indices.

In more detail there may be included various poly-functional groups in order to obtain cross-linked polymers which have

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greater resistance to moisture ingress, temperature stability, and ageing stability. In general, suitable di-functional monomers which may be used have the general formula (III)

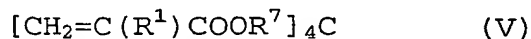
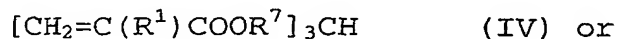


5 wherein R^5 and $\text{R}^{5'}$ are H or CH_3 and could be same or different and R^6 and $\text{R}^{6'}$ are C1 to C12 aliphatic or aromatic organic groups and can also be the same or different. Preferred examples of such di-functional compounds which are unsubstituted are:

10 1,4-butanediol diacrylate, ethylene diacrylate, ethoxylated bisphenol A diacrylate, bisphenol A diacrylate or dimethacrylate, neopentylglycol diacrylate, diethyleneglycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexane-diol diacrylate, triethylene glycol diacrylate or dimethylacrylate;
15 tetraethylene glycol diacrylate or dimethacrylate; polyethylene glycol diacrylate or dimethacrylate; dipropylene glycol diacrylate; tripropylene glycol diacrylate; ethoxylated neopentyl glycol diacrylate; propoxylated neopentyl glycol diacrylate, and mixtures of two or more thereof.

20

Suitable tri- and tetra-functional acrylate monomers which may be used generally have the general formula (IV) or (V).



25 wherein in each of formulae IV and V, all the R^1 and/or all the R^7 groups may be the same or may be different, R^1 having the same meaning as before, and R^7 being a C1 to C12 aliphatic or aromatic group.

30 Preferred examples of such tri- and tetra-functional acrylates are:

pentaerythritol triacrylate, trimethylolpropane trimethacrylate, trimethylol propane triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated

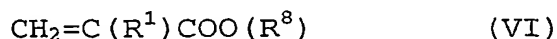
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trimethylolpropane triacrylate, glyceryl propoxylated triacrylate, *tris* (2-hydroxyethyl) isocyanurate triacrylate, pentaerythritol tetracrylate, alkoxyated tetracrylate, ditrimethylolpropane tetracrylate and mixtures thereof.

5

Where such polyfunctional acrylates are included, they may conveniently be used in amounts corresponding to up to 100% and preferably at least 20% w/w of non-sulphur containing monomer units which are di-functional and/or up to 30% of tri-
10 and/or tetra-functional monomer units, with desirably at least 10% w/w, advantageously at least 30% w/w, for example, from 30 to 50% w/w, of all non-sulphur containing monomer units used, being polyfunctional.

15 There may also be used acrylate monomers whose main function is as low-cost extenders (although it will of course be appreciated that various monomers used in the present invention, may have two or more different roles). Suitable mono-functional monomers in this connection are of the general
20 formula (VI).



wherein R^1 has the same meaning as before (preferably is CH_3) and R^8 is a C1 to C12 aliphatic or aromatic organic group.

25 Preferred examples of such compounds are: methyl methacrylate, benzyl methacrylate, phenyl methacrylate, trimethylcyclohexyl methacrylate, methacrylic acid, α - and β - naphthyl
methacrylate, isobutyl methacrylate, methyl α -chloroacrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl acrylate, 2-
30 hydroxyethyl acrylate, 2-hydroxypropyl acrylate, cyclohexyl acrylate; phenoxyethyl acrylate; β -carboxylethyl acrylate; isobornyl acrylate; tetrahydrofurfuryl acrylate; propylene glycol monoacrylate; 2-(2-ethoxyethoxy)ethyl acrylate, cyanoethoxyethyl acrylate, cyclohexymethacrylate,

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cyclohexylacrylate, adamantyl methacrylate and mixtures thereof.

Conveniently up to 25% w/w of the non-sulphur containing monomer units in the photo-polymer may be of this type.

It will also be appreciated that the monomers used may be substituted to a greater or lesser degree. In this connection it may be noted that reducing the number of C-H bonds present in the photo-polymer is beneficial in reducing absorption losses - especially at longer wavelengths such as 1.55µm. Particularly preferred substituents in this connection are Deuterium and the halogens, in particular F, Cl and Br. In general up to 95% w/w, preferably 50 to 80% w/w, for example up to 78% w/w, of the monomer units may have one or more such substituents.

Preferred examples of such monomers are: chloroethyl acrylate, hexafluorobutyl methacrylate, trichloroethyl acrylate, trichloroethyl methacrylate, trifluoroethyl acrylate, hexafluoro bisphenol A diacrylate, tetrachloro bisphenol A diacrylate, pentafluorobenzyl-acrylate or methacrylate, pentachlorophenyl acrylate or methacrylate, pentafluorophenyl acrylate or methacrylate, perfluorocyclopropyl acrylate, perfluorocyclobutyl acrylate, perfluorocyclophenyl acrylate, perfluorocyclohexyl acrylate, perfluorocyclobutyl methacrylate, perfluorocyclohexyl methacrylate, 1-hydroperfluorocyclohexyl acrylate, perfluorodecyl-acrylate, methacrylate, hexafluoro isopropyl (meth)acrylate, perfluoronorbornylmethyl (meth)acrylate, perfluoroisobornyl (meth)acrylate, hexafluoropentandiyl-1,5-bis (meth)acrylate, perfluoroethyleneglycol di(meth)acrylate, poly perfluoroethyleneglycol di(meth)acrylate, hexafluoro ethoxylated bisphenol A di(meth)acrylate, tetrachloro

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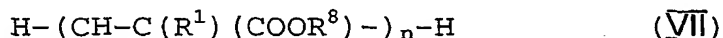
ethoxylated bisphenol A di(meth)acrylate, tetrabromo
ethoxylated bisphenol A di(meth)acrylate, dodecafluoroheptyl
(meth)acrylate, eicosafluoroundecyl (meth)acrylate,
heptadecafluorodecyl (meth)acrylate, hexadecafluorononyl
5 (meth)acrylate, heptadecafluorodecyl (meth)acrylate,
hexadecafluorononyl (meth)acrylate, octafluoropentyl
(meth)acrylate, perfluoroheptoxy
poly(propyloxy) (meth)acrylate, perfluorocyclohexyl-1,4-
dimethyl methacrylate, perfluoroethyleneglycol
10 di(meth)acrylate, hexafluoro-bisphenol A di(meth)acrylate,
tetrafluorobutanediol di(meth)acrylate, octafluorohexanediol-
1,6-diacrylate and mixtures of two or more thereof.

In accordance with the present invention it is generally more
15 or less readily possible to use either of the acrylate and
corresponding methacrylate compounds depending on the detailed
desired characteristics of the production process and/or
product. In general the acrylate compounds will polymerize
more quickly being more reactive, whilst the corresponding
20 methacrylate compounds will generally provide less opaque and
more thermally stable products. Accordingly the present
invention extends to and includes compounds corresponding to
those identified in the foregoing and hereinbelow, wherein the
acrylate moiety may be substituted for by a corresponding
25 methacrylate moiety and vice versa, for example a reference to
pentaerythritol triacrylate is intended to include a reference
to pentaerythritol tri-(methyl acrylate) unless otherwise
indicated or inappropriate in the particular context thereof.
Furthermore, in some instances (for the sake of brevity) we
30 have used the terminology "(meth)acrylate" to denote each of
the acrylate and corresponding methacrylate compounds.

In order to increase the viscosity of the polymerisable
compositions, especially where it is desired to fabricate

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thicker circuit components using manufacturing processes such as spinning, part of the monomer content may be pre-polymerized and present in the composition as polyacrylate polymer. Thus there may be included in the photo-polymerisable composition, a polyacrylate polymer of the general formula (VII):



wherein R^1 has the same meaning as before, R^8 is C_1 to C_{10} , optionally substituted, for example by halo, alkyl or aryl, and n is an integer greater than 100, typically n is in the range of from 200 to 50,000. Conveniently up to 15% w/w of the monomer units in the photo-polymer may be incorporated in this way.

Preferred examples of such polymers are: poly(methyl methacrylate), poly(phenyl methacrylate), poly(benzyl methacrylate), poly(butyl acrylate), poly(ethylene glycol dimethacrylate), poly(isopropyl) methacrylate and poly(ethyl methacrylate), and halogenated analogues thereof including for example, poly(trifluoroethyl methacrylate), poly(pentachlorophenyl methacrylate) and poly(pentabromophenyl methacrylate).

Where non-acrylate monomers are included, these may conveniently constitute up to 40% w/w of the total monomer. Suitable non-acrylate monomers that may be used include one or more of epoxide, polycarbonate, silicone and siloxane compounds.

Various photo-initiators suitable for use in polymerisation are well known in the art. In general there may be used from 0.1 to 5% w/w of photo-initiator in the photo-polymerisable compositions. Suitable photoinitiators that may be mentioned are : benzidimethyl ketal (Irgacure 651 TRADE NAME); alpha,

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alpha diethyloxy acetophenone; alpha, alpha-dimethyloxy-alpha hydroxy acetophenone (Darocur 1173, TRADE NAME); 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, TRADE NAME), 1-[4-(2-hydroxyethoxy) phenyl]-2-hydroxy-2-methyl-propan-1-one (Darocur 2959, TRADE NAME); 2-methyl-1-4(methylthio) phenyl]-2-morpholino-propan-1-one (Irgacure 907, TRADE NAME); and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl) butan-1-one (Irgacure 369, TRADE NAME), 50% benzophenone and 50% 1-hydroxy-cyclohexyl-phenyl ketone (Irgacure 500, TRADE NAME).

10

Various other additives known in the photo-polymer art may also be included in the photo-polymeriseable compositions. Thus, for example, it is generally desirable to include a so-called adhesion promoter to increase adhesion of the photo-
15 polymer, especially in the cladding layer, to the substrate and prevent lifting-off thereof during washing away of unpolymerised composition after photo-polymerisation and/or in subsequent use. Typically the photo-polymeriseable composition may include from 0 to 10% w/w of adhesion
20 promoter, preferably from 5 to 8 wt%. Examples of suitable adhesion promoters are: 3-(trimethoxysilyl)propyl methacrylate, 3-acryloxypropyl trichlorosilane, trimethylsilyl propyl methacrylate, and 3-amino propyl triethoxysilane.

25 In general the preparation, processing and use of the photo-polymerisable compositions of the present invention are similar to those conventionally employed in the art. Thus in order to ensure substantial homogeneity of the photo-polymerisable compositions (and ultimately the photo-
30 polymers), the various components are thoroughly mixed together for a suitable period of time, typically from 0.05 to 250 hours, conveniently from 0.5 to 50 hours. Desirably mixing is carried out at a somewhat elevated temperature - generally from 20 to 80°C.

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Prior to polymerisation, the composition is desirably filtered, conveniently using a pore size of from 0.1 to 10 μ m.

5 Application of the polymerizable composition to a suitable substrate such as glass, silica, silicon, etc, may be effected using any suitable technique known in the art, such as dip, spin, spray, flow or slot coating methods, further details of which are described in the literature.

10

For the purposes of producing PLCs, the photo-polymerisable composition coating is exposed to UV-light through a mask containing the various optical component structures required such as waveguides, couplers, splitters and gratings under
15 suitable conditions for a suitable time interval in accordance with normal practice, after which the unexposed regions are washed away using suitable organic solvents such as acetone, *iso*-butyl methyl ketone or mixtures thereof with *iso*-propanol. This leaves ridge-like photo-polymer structures on the
20 substrate.

Normally, a second coating layer (usually referred to as the cladding layer), having a refractive index somewhat lower, typically from 0.3 to 8% less than that of the first layer, is
25 applied over the top of the substrate with the laid-down photo-polymer structures thereon, conveniently by spinning, and then cured.

It will of course be appreciated that the optical polymers of
30 the present invention may also be produced by means of thermal polymerisation of the monomer(s), although this is generally less convenient. In order to produce photonic components such as PLCs and/or other devices, the polymers so obtained would normally be patterned using photolithography and reactive ion

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etching techniques well known in the art. In such cases it will be appreciated that there should be used suitable thermally activatable initiators in place of the photo-initiators.

Various thermally activated initiators suitable for use in polymerisation are well known in the art. In general there may be used from 0.1 to 5% w/w of a thermally activated initiator in the polymerisable compositions. Suitable thermally activated initiators which may be mentioned include 2-2'azo-bis-isobutyrylnitrile (AIBN) and benzoyl peroxide. In general polymerization would be carried out at an elevated temperature of up to 200°C, conveniently about 100°C.

The invention is further illustrated by the following examples, which are illustrative of the specific aspects of practising the invention and should not be taken as limiting the scope of the invention to be defined by the claims. In the following examples, thermal stability was determined using thermogravimetric methods, with substantial thermal stability being indicated by weight loss of not more than 0.5% w/w. T_g Glass transition temperature measurements were determined using dynamic mechanical methods in cantilever mode, at a heating rate of 5°C per minute (see for example "TA Instruments, Thermal Analysis & Rheology Operators Manual", 1999).

25

Example 1: Preparation of Photo-polymerisable Composition and Production of PLC.

2.00 g phenylthioethyl acrylate (from Bimax, Maryland) was added to 2.00 g methyl methacrylate (from Sigma - Aldrich) and 1.25 g ethoxylated bisphenol A dimethacrylate (from Roehm GmbH, Darmstadt) and thoroughly mixed. 0.25 g polymethyl methacrylate powder was added to this solution and dissolved by stirring at 60°C for 12 h. This mixture was further reacted for 96 h at 60°C. 0.1838 g photo-initiator (Irgacure 184

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(TRADE NAME) from Ciba Specialty Chemicals) was also added to the above mixture and dissolved. This solution was filtered using a 1 μ m glass pre-filter and 0.2 μ m Teflon (TRADE NAME) filter and spun on glass or Si substrate. The spinning speed (rpm) was kept 340 for 10 sec and 560 for 30 sec. This coating was placed on a computer controlled translation stage and tracks were defined by exposing it with a focused 4 mW power of 325 nm He-Cd UV laser. The unpolymerised parts were washed off by rinsing the substrate with isobutyl methyl ketone for 2 min. The ridge-like structures of the PLC formed on the substrate were covered using a coating from a second formulation synthesised exactly as above but with the following composition: 1.00 g phenylthioethyl acrylate + 2.00 g methyl methacrylate + 1.00 g ethoxylated bisphenol A dimethacrylate + 0.25 g polymethyl methacrylate + 0.14 g Irgacure 184 (TRADE NAME). This layer was flooded with UV light from a mercury lamp for 1 h which led to polymerisation of the monomer layer and provided a PLC with clad waveguides having transmission losses of 0.17 dB/cm at 850 nm. The photo-polymer of the PLC was stable up to 300°C

Example 2:

3.25 g phenylthioethyl acrylate was added to 0.75 g methyl methacrylate. 0.50 g ethylene diacrylate (from Fluka) and 0.5g pentaerythritol tetracrylate (from ABCR) were also added to the above mixture and thoroughly mixed. 0.40 g polymethyl methacrylate powder was added to this solution and dissolved by stirring at 60°C for 12 h. This mixture was further reacted for 96 h at 60°C. 0.15 g Irgacure 184 (TRADE NAME) photoinitiator was also added to the above mixture and dissolved. This solution was filtered using 0.2 micron Teflon (TRADE NAME) filter and 1 μ m glass pre-filter and spun on glass or Si substrate. The spinning speed (rpm) was kept to 340 for 10 sec and 560 for 30 sec. This coating also was structured in

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a similar manner as explained in Example 1. The following composition was used for the cladding layer. 2.25 g phenylthioethyl acrylate + 2.00 g methyl methacrylate + 0.50 g ethylene diacrylate + 0.5 g pentaerythritol tetracrylate + 0.42 g polymethyl methacrylate powder + 0.158 g Irgacure 184 (TRADE NAME). This resulted in cladded planar waveguides with transmission losses of 0.5 dB/cm at 1300 nm and thermal stability of up to 275°C.

10 Example 3:

1.82 g phenylthioethyl acrylate was added to 0.328 g methyl methacrylate. 0.37 g ethylene diacrylate, 0.385 g pentaerythritol tetracrylate and 1.094 g hexafluorobutyl methacrylate (from Sigma-Aldrich) were also added to the above mixture and thoroughly mixed. 0.30 g polymethyl methacrylate powder was added to this solution and dissolved by stirring at 40°C for 24 h. This mixture was further reacted for 48 h at 40°C. 0.10 g Irgacure 184 (TRADE NAME) was also added to the above mixture and dissolved. This solution was filtered and spun on glass or Si substrate. This coating also was structured in a similar manner as explained in Example 1. The following composition was used for the cladding layer. 0.82g phenylthioethyl acrylate + 1.328 g methyl methacrylate + 0.47g ethylene diacrylate + 0.285 g pentaerythritol tetracrylate + 1.2 g hexafluorobutyl methacrylate + 0.30 g poly(methyl methacrylate) + 0.15 g Irgacure 184 (TRADE NAME). This resulted in planar waveguides with low transmission losses of 0.7 dB/cm at 1550 nm.

30 Example 4:

2.25 g phenylthioethyl acrylate was added to 0.55 g methyl methacrylate. 0.90 g ethoxylated bisphenol A dimethacrylate, 0.50 g pentaerythritol tetracrylate and 1.51 g pentachlorophenyl methacrylate (from Sigma-Aldrich) were also

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added to the above mixture and thoroughly mixed. 0.143 g polymethyl methacrylate powder was added to this solution and dissolved by stirring at 50°C for 24 h. This mixture was further reacted for 48 h at 60°C. 0.143 g Irgacure 184 (TRADE NAME) was also added to the above mixture and dissolved. This solution was filtered and spun on to a glass or Si substrate. This coating also was structured as in Example 1 in order to obtain a PLC with an array of planar waveguides each having a height of 7µm and a width of 7 µm. Cladding layer was applied as above using the following composition: 1.95 g phenylthioethyl acrylate + 1.14 g methyl methacrylate + 1.22 g ethoxylated bisphenol A dimethacrylate + 0.48 g pentaerythritol tetracrylate + 1.21 g pentachlorophenyl methacrylate + 0.27 g polymethyl methacrylate + 0.15 g Irgacure 184 (TRADE NAME). This resulted in planar waveguides with low transmission losses of 0.5 dB/cm at 1550 nm.

Example 5:

1.0g phenylthioethyl acrylate was added to 1.25g bisphenol A dimethacrylate (from Sigma-Aldrich) and 2.75g hexane dimethacrylate (from Sigma-Aldrich) and thoroughly mixed. 0.20g polymethyl methacrylate powder was added to this solution and dissolved by stirring at 60°C for 24 hours. 0.1g Darocur 1173 (TRADE NAME) photoinitiator was added to the above mixture and dissolved for 1 hour. This solution was then filtered using a 0.2 micron Teflon (TRADE NAME) filter and spun on glass or Si substrate. The spinning speed was kept at 150rpm for 10 seconds and 300 for 20 seconds. This layer was flooded with UV light from a mercury lamp for 5 min, which led to polymerisation of the monomer, and subjected to a post-cure at a temperature of 150°C for 1 hour. This photopolymer has a glass transition temperature of 203°C and is thermally stable up to 300°C.

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Example 6:

1.0g phenylthioethyl acrylate was added to 1.0g ethoxylated bisphenol A dimethacrylate and 3.0g hexane dimethacrylate (from Sigma-Aldrich) and thoroughly mixed. 0.20g polymethyl methacrylate powder was added to this solution and dissolved by stirring at 60°C for 24 hours. 0.1g Darocur 1173 (TRADE NAME) photoinitiator was added to the above mixture and dissolved for 1 hour. This solution was then filtered using a 0.2 micron Teflon (TRADE NAME) filter and spun on glass or Si substrate. The spinning speed was kept at 150rpm for 10 seconds and 300 for 20 seconds. This layer was flooded with UV light from a mercury lamp for 5 min., which led to polymerisation of the monomer, and subjected to a post-cure at a temperature of 150°C for 1 hour. This photo-polymer has a glass transition temperature of 159°C and is stable up to 300°C.

Example 7:

1.0g thiodiglycoldiacrylate (from Bimax, Maryland) was added to 0.5g hexafluorobisphenol A dimethacrylate (from ABCR of Karlsruhe, Germany), 1.75g octafluorohexane diemthacrylate (from Apollo Scientific Ltd of Whaley Bridge, England) and 1.75g perfluorocyclohexane dimethyl dimethacrylate (from Apollo) and thoroughly mixed. 0.20g polymethyl methacrylate powder was added to this solution and dissolved by stirring at 60°C for 24 hours. 0.1g Darocur 1173 (TRADE NAME) photoinitiator was added to the above mixture and dissolved for 1 hour. This solution was then filtered using a 0.2 micron Teflon (TRADE NAME) filter and spun on glass or Si substrate. The spinning speed was kept at 150rpm for 10 seconds and 300 for 20 seconds. This coating was structured as in example 1 to produce a highly fluorinated waveguide structure which is thermally stable up to 300°C.

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CLAIMS

1. An optical polyacrylate polymer wherein at least 20%
w/w of the total monomer repeating units are of the general
5 formula (I)



wherein R^1 is H or a C1 to C12 aliphatic and/or aromatic group,
and R^2 is an aliphatic and/or aromatic moiety containing at
least one S atom.

10

2. A polymer according to claim 1 wherein R^1 is H or a C1 to
C6 aliphatic and/or aromatic group.

3. A polymer according to claim 2 wherein R^1 is H or CH_3 .

15

4. A polymer as claimed in any one of claims 1 to 3 wherein R^2
is of the general formula R^3SR^4 wherein, R^3 and R^4 are the same
or different and each is selected from an aliphatic group
 $\text{C}_n\text{H}_{2n+1-y}\text{Z}_y$ wherein n is an integer from 1 to 12, the or each Z
20 can be F, Cl, Br, I or (meth)acrylate, and y is from 0 to
2n+1, and an aromatic group $\text{C}_6\text{H}_{4-x}\text{A}_x$, wherein the or each A can
be F, Cl, Br or I and x is a natural number from 0 to 5.

5. A polymer as claimed in claim 4 wherein n is from 1 to 6.

25

6. A polymer as claimed in either one of claims 4 and 5
wherein x is zero.

7. A polymer as claimed in any one of claims 4 to 6 wherein R^2
30 is selected from sulphur containing moieties including:

$(\text{C}_6\text{H}_5)\text{S}(\text{CH}_2)$, $(\text{C}_6\text{H}_5)\text{S}(\text{C}_2\text{H}_4)$, $(\text{C}_6\text{H}_5)\text{S}(\text{C}_6\text{H}_4)$, $(\text{CH}_3)\text{S}(\text{CH}_2)$,
 $(\text{CH}_3)\text{S}(\text{C}_2\text{H}_4)$, $(\text{CH}_3)\text{S}(\text{C}_6\text{H}_4)$, $(\text{C}_2\text{H}_5)\text{S}(\text{CH}_2)$, $(\text{C}_2\text{H}_5)\text{S}(\text{C}_2\text{H}_4)$ and
 $(\text{C}_2\text{H}_5)\text{S}(\text{C}_6\text{H}_4)$.

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8. A polymer as claimed in any one of claims 4 to 6 wherein R^2 is selected from the group comprising: $(CH_2)S(CH_2-OOC-C(R^1)=CH_2)$, $(C_2H_4)S(C_2H_4-OOC-C(R^1)=CH_2)$ and $(C_3H_6-S-C_3H_6-OOC-C(R^1)=CH_2)$.

5

9. A polymer as claimed in any one of claims 1 to 8 wherein at least 20% w/w of the total monomer repeating units are from a monomer of the general formula (II): $CH_2=C(R^1)COOR^2$ (II) wherein R^1 and R^2 have the same meaning as before.

10

10. A polymer as claimed in any one of claims 1 to 9 wherein at least 10 % w/w of said total monomer units are from one or more poly-functional monomers wherein said poly-functional monomers are selected from di-, tri and tetra-functional

15 monomers.

11. A polymer as claimed in claim 10 wherein said di-functional monomer(s) has the general formula (III)

$CH_2=C(R^5)COO R^6-R^{6'}OOC(R^{5'})C=CH_2$; wherein, R^5 and $R^{5'}$ are H or CH_3

20 and could be same or different and R^6 and $R^{6'}$ are C1 to C12 aliphatic or aromatic organic groups and can also be the same or different.

12. A polymer as claimed in claim 11 wherein said di-

25 functional monomer(s) is selected from: 1,4-butanediol

diacrylate, ethylene diacrylate, ethoxylated bisphenol A

diacrylate, bisphenol A diacrylate or dimethacrylate,

neopentylglycol diacrylate, diethyleneglycol diacrylate,

diethylene glycol dimethacrylate, 1,6-hexane-diol diacrylate,

30 triethylene glycol diacrylate or dimethylacrylate;

tetraethylene glycol diacrylate or dimethacrylate;

polyethylene glycol diacrylate or dimethacrylate; dipropylene

glycol diacrylate; tripropylene glycol diacrylate; ethoxylated

neopentyl glycol diacrylate; propoxylated neopentyl glycol

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diacrylate, perfluorocyclohexyl-1,4-dimethyl methacrylate, perfluoroethyleneglycol diacrylate, hexafluoro-bisphenol A diacrylate, tetrafluorobutanediol diacrylate, octafluorohexanediol-1,6-diacrylate and mixtures thereof.

5

13. A polymer as claimed in any one of claims 10 to 12 wherein said tri-functional monomer(s) has the general formula (IV), $[\text{CH}_2=\text{C}(\text{R}^1)\text{COOR}^7]_3\text{CH}$; wherein, R^1 has the same meaning as before and R^7 is a C1 to C12 aliphatic or aromatic group.

10

14. A polymer as claimed in claim 13 wherein said tri-functional monomer is selected from: pentaerythritol triacrylate, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, ethoxylated trimethylolpropane

15 triacrylate, propoxylated trimethylolpropane triacrylate, *tris* (2-hydroxyethyl) isocyanurate triacrylate, and glyceryl propoxylated triacrylate and mixtures thereof.

15. A polymer as claimed in any one of claims 10 to 14
20 wherein said tetra-functional monomer(s) has the general formula (V) $[\text{CH}_2=\text{C}(\text{R}^1)\text{COOR}^7]_4\text{C}$, wherein R^1 and R^7 have the same meaning as before.

16. A polymer as claimed in claim 15 wherein said tetra-
25 functional monomer(s) is selected from: pentaerythritol tetracrylate, alkoxylated tetracrylate, ditrimethylolpropane tetracrylate and mixtures thereof.

17. A polymer as claimed in any one of claims 1 to 16 wherein
30 at least 10% of the monomer units are from non-sulphur containing monomers of the general formula (VI)
 $\text{CH}_2=\text{C}(\text{R}^1)\text{COO}(\text{R}^8)$.

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18. A polymer as claimed in claim 17 wherein said non-sulphur containing monomers are selected from: methyl methacrylate, benzyl methacrylate, phenyl methacrylate, trimethylcyclohexyl methacrylate, methacrylic acid, α - and β - naphthyl methacrylate, isobutyl methacrylate, methyl α -chloroacrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, cyclohexyl acrylate; phenoxyethyl acrylate; β -carboxylethyl acrylate; isobornyl acrylate; tetrahydrofurfuryl acrylate; propylene glycol monoacrylate; 2-(2-ethoxyethoxy)ethyl acrylate, cyanoethoxyethyl acrylate, cyclohexymethacrylate, cyclohexylacrylate, adamantyl methacrylate and mixtures thereof.
19. A polymer as claimed in any one of claims 17 and 18 wherein up to 25 % w/w of the total monomer units forming the polymer are from non-sulphur containing monomers of said general formula (VI).
20. A polymer as claimed in claim 19 wherein up to 95 % w/w of the non-sulphur containing monomers of formula (VI) are halo-substituted.
21. A polymer as claimed in claim 20 wherein said halo-substituted monomers are selected from: chloroethyl acrylate, hexafluorobutyl methacrylate, trichloroethyl acrylate, trichloroethyl methacrylate, trifluoroethyl acrylate, hexafluoro bisphenol A diacrylate, tetrachloro bisphenol A diacrylate, pentafluorobenzyl-acrylate or methacrylate, pentachlorophenyl (meth)acrylate, pentafluorophenyl acrylate or methacrylate, perfluorocyclopropyl acrylate, perfluorocyclobutyl acrylate, perfluorocyclophenyl acrylate, perfluorocyclohexyl acrylate, perfluorocyclobutyl methacrylate, perfluorocyclohexyl methacrylate, 1-

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hydroperfluorocyclohexyl acrylate, perfluorodecyl-acrylate, methacrylate, hexafluoro isopropyl (meth)acrylate, perfluoronorbornylmethyl (meth)acrylate, perfluoroisobornyl (meth)acrylate, hexafluoropentandiyl-1,5-bis (meth)acrylate, 5 perfluoroethyleneglycol di(meth)acrylate, poly perfluoroethyleneglycol di(meth)acrylate, hexafluoro ethoxylated bisphenol A di(meth)acrylate, tetrachloro ethoxylated bisphenol A di(meth)acrylate, tetrabromo ethoxylated bisphenol A di(meth)acrylate, dodecafluoroheptyl 10 (meth)acrylate, eicosafluoroundecyl (meth)acrylate, heptadecafluorodecyl (meth)acrylate, hexadecafluorononyl (meth)acrylate, heptadecafluorodecyl (meth)acrylate, hexadecafluorononyl (meth)acrylate, octafluoropentyl (meth)acrylate and perfluoroheptoxy 15 poly(propyloxy) (meth)acrylate wherein (meth) denotes either the acrylate or the corresponding methacrylate derivative.

22. A polymer as claimed in any one of claims 1 to 21 having a T_g value of at least 180°C.

20

23. A polymer as claimed in any one of claims 1 to 22 thermal stability up to at least 280°C.

24. A photo-polymerisable composition comprising acrylate 25 monomer in intimate admixture with a photo-initiator, wherein at least 20% w/w of the acrylate monomer is of the general formula (II)



wherein R^1 is H or a C1 to C12 aliphatic and/or aromatic group, 30 and R^2 is an aliphatic and/or aromatic moiety containing at least one S atom.

25. A process for producing a polyacrylate photo-polymer comprising the steps of :

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providing a photo-polymerizable composition of claim 24,
and exposing said composition to light so as to activate the
photo-initiator.

- 5 26. A method of producing a planar light-wave circuit
comprising the steps of :
applying a photo-polymerisable composition of claim 24 to a
substrate;
projecting a photographic image defining components of said
10 planar light-wave circuit onto said composition so as to
photo-polymerise selected portions of said composition to
produce a polymer of claim 1; and
removing unreacted composition from said substrate.
- 15 27. A method as claimed in claim 26 wherein a second coating
layer having a refractive index lower than that of the
photopolymer is applied over the top of the substrate with the
laid-down photo-polymer structures thereon; and then cured.
- 20 28. An optical polyacrylate polymer obtainable by
polymerisation of acrylate monomer wherein at least 20% w/w of
the acrylate monomer is of the general formula (II)
$$\text{CH}_2=\text{C}(\text{R}^1)\text{COOR}^2 \quad (\text{II})$$

wherein R^1 and R^2 have the same meaning as before.
- 25 29. A planar lightwave circuit wherein the circuitry is
formed of a polymer according to any one of claims 1 to 23.

INTERNATIONAL SEARCH REPORT

Intern Application No

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 765 879 A (ESSILOR INT) 15 January 1999 (1999-01-15) page 4, line 24 -page 5, line 16; claims 1,3	1-3, 24
A	EP 0 384 725 A (TORAY INDUSTRIES) 29 August 1990 (1990-08-29) the whole document	1-3, 24

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

information on patent family members

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